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Transition probabilities for spontaneous emission in the adiabatic and nonadiabatic approximations for all bound vibrational levels of the $E,F\,^1\Sigma_g^+$, $G,K\,^1\Sigma_g^+$, and $H,\bar{H}\,^1\Sigma_g^+$ states of H_2

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The vibrational dipole transition moment integrals are calculated for the individual v',v'' bands of the $E,F\,^1\Sigma_g^+$, $G,K\,^1\Sigma_g^+$, $H,\bar{H}\,^1\Sigma_g^+-B\,^1\Sigma_u^+$, $B'\,^1\Sigma_u^+$, $C\,^1\Pi_u$ systems on the basis of the R-dependent *ab initio* electronic transition dipole moments of Wolniewicz and Dressler. Nonadiabatic effects are included for the transition probabilities and lifetimes by the representation of the nonadiabatic wave functions of all bound vibrational $^1\Sigma_g^+$ ($J=0$) levels in the adiabatic basis of the E,F, G,K, and $H,\bar{H}$ electronic states. Wherever possible the calculated lifetimes are compared with experimental results.

I. INTRODUCTION

The radiative lifetimes of the lowest excited singlet *gerade* states of H_2 are determined by their radiation into the states $B\,^1\Sigma_u^+$, $B'\,^1\Sigma_u^+$ and $C\,^1\Pi_u$. These lifetimes as well as the individual vibrational transition probabilities $A_{iv',fv''}$ are of interest in the interpretations of measurements of lifetimes,[1-4] emission cross sections,[5] and astronomical spectra.[6] The theoretical electronic dipole transition moments $M_{i,f}(R)$ have been found to depend strongly on internuclear distance R.[7,8] Therefore, the Franck-Condon approximation would be very inaccurate. We compute the vibrational transition moment integrals in the adiabatic approximation and, using appropriate eigenvectors, we transform these to account for the nonadiabatic interaction between the $E,F\,^1\Sigma_g^+$, $G,K\,^1\Sigma_g^+$, and $H,\bar{H}\,^1\Sigma_g^+$ states for $J=0$.

II. BORN-OPPENHEIMER AND ADIABATIC APPROXIMATIONS

The vibrational transition moment integrals connecting the initial electronic state i with the final electronic state f,

$$M_{iv',fv''}=\int F_{iv'}(R)M_{i,f}(R)F_{fv''}(R)dR \ , \tag{1}$$

were computed using cubic spline interpolations of the electronic dipole moment functions $M_{i,f}(R)$.[7,8] The vibrational functions $F(R)$ were calculated by numerical integration using the Numerov method, from the most accurate *ab initio* potential-energy curves available. The clamped-nuclei or "Born-Oppenheimer" electronic energies are from Refs. 9 and 10 (E,F), 10 (G,K), 11 ($H,\bar{H}$), 12 (B), 13 (B'), 14 (C), and the diagonal or "adiabatic" corrections for nuclear motion are from Refs. 9 (E,F), 10 (G,K), 15 ($H,\bar{H}$), 16 (B), and 17 (B'), and 18 (C). The integrations (1) were performed between lower and upper limits of $R=0.4$ and 19.0 a.u. with steps of 0.0125 a.u.

The probability for spontaneous emission of the $iv'\rightarrow fv''$ transition is given in (a.u.) by

$$A_{iv',fv''}=\tfrac{4}{3}\alpha^3(E_{iv'}-E_{fv''})^3 g'' M_{iv',fv''}^2 \ , \tag{2}$$

where α is the fine-structure constant, the energies E and transition moment M are in a.u., and the statistical weight factor $g''=2-\delta_{0,\Lambda''}$ is equal to unity for $^1\Sigma_g^+$-$^1\Sigma_u^+$ transitions and equal to two for $^1\Sigma_g^+$-$^1\Pi_u$ transitions; this is consistent with the choice of transition moment operators in the computations of $M_{i,f}(R)$,[7,8] and it would imply summation over P, Q, and R lines if initial levels with $J'>0$ were considered. In this form Eq. (2) allows for the v',v'' dependence of the transition energies while neglecting their J',J'' dependence.

The atomic unit of frequency is equal to $\alpha c/a_0 =4.134\,137\times10^{16}\ \text{s}^{-1}$ such that Eq. (2) is equivalent to

$$A_{iv',fv''}(\text{s}^{-1})=2.142\times10^{10}(E_{iv'}-E_{fv''})^3 g'' M_{iv',fv''}^2 \ . \tag{3}$$

The radiative lifetime $\tau_{iv'}$ of the initial level iv' is given by

$$1/\tau_{iv'}=A_{iv'}=\sum_{f,v''}A_{iv',fv''} \ . \tag{4}$$

This summation includes all vibrational levels v'' of all electronic states f accessible in emission from the level i,v'. Continua are not accessible from the levels considered in this paper.

The resulting values $A_{iv'}$ and $\tau_{iv'}$ are presented together with the partial transition probabilities

$$A_{iv',f}=\sum_{v''}A_{iv',fv''} \tag{5}$$

in Table I. The results obtained with oscillator functions $F(R)$ computed from uncorrected clamped-nuclei potential energies are designated "Born-Oppenheimer"; those from potential functions including the adiabatic corrections are designated "adiabatic."

TABLE I. Partial and total transition probabilities (s^{-1}) and lifetimes (s). Top entry, nonadiabatic; middle entry, adiabatic; bottom entry, Born-Oppenheimer approximation. The correlation between the vibronic level index k with spectroscopic labels is defined and tabulated in Sec. III. Numbers in parentheses indicate factors of 10, e.g., $0.5(+2)=0.5\times10^2$.

K	$A(K-B)$	$A(K-C)$	$A(K-B')$	A	T
1	0.4933(+7)	0.1447(+3)	0.0	0.4933(+7)	0.2027(−6)
	0.4935(+7)	0.1455(+3)	0.0	0.4935(+7)	0.2026(−6
	0.5055(+7)	0.0	0.0	0.5055(+7)	0.1978(−6)
2	0.8740(+6)	0.5230(−3)	0.0	0.8740(+6)	0.1144(−5)
	0.8760(+6)	0.7660(−3)	0.0	0.8760(+6)	0.1142(−5)
	0.8801(+6)	0.4731(−3)	0.0	0.8801(+6)	0.1136(−5)
3	0.1506(+7)	0.9500(−3)	0.0	0.1506(+7)	0.6640(−6)
	0.1508(+7)	0.8390(−3)	0.0	0.1508(+7)	0.6629(−6)
	0.1522(+7)	0.5874(−3)	0.0	0.1522(+7)	0.6569(−6)
4	0.7188(+7)	0.7378(+4)	0.0	0.7196(+7)	0.1390(−6)
	0.7185(+7)	0.7391(+4)	0.0	0.7192(+7)	0.1390(−6)
	0.7325(+7)	0.6777(+4)	0.0	0.7332(+7)	0.1364(−6)
5	0.2208(+7)	0.1834(+2)	0.0	0.2208(+7)	0.4530(−6)
	0.2208(+7)	0.2371(+2)	0.0	0.2208(+7)	0.4528(−6)
	0.2252(+7)	0.3337(+2)	0.0	0.2252(+7)	0.4440(−6)
6	0.3154(+7)	0.1586(+2)	0.0	0.3154(+7)	0.3171(−6)
	0.3161(+7)	0.2081(+2)	0.0	0.3161(+7)	0.3163(−6)
	0.3313(+7)	0.2976(+2)	0.0	0.3313(+7)	0.3018(−6)
7	0.1005(+8)	0.5653(+4)	0.0	0.1005(+8)	0.9947(−7)
	0.9965(+7)	0.5676(+4)	0.0	0.9970(+7)	0.1003(−6)
	0.9988(+7)	0.4379(+4)	0.0	0.9992(+7)	0.1001(−6)
8	0.3910(+7)	0.2170(+4)	0.0	0.3912(+7)	0.2556(−6)
	0.3924(+7)	0.2457(+4)	0.0	0.3927(+7)	0.2547(−6)
	0.4169(+7)	0.2681(+4)	0.0	0.4172(+7)	0.2397(−6)
9	0.5688(+7)	0.2446(+4)	0.0	0.5690(+7)	0.1757(−6)
	0.5606(+7)	0.2654(+4)	0.0	0.5609(+7)	0.1783(−6)
	0.5685(+7)	0.3278(+4)	0.0	0.5689(+7)	0.1758(−6)
10	0.7600(+7)	0.4344(+4)	0.0	0.7604(+7)	0.1315(−6)
	0.7630(+7)	0.4591(+4)	0.0	0.7634(+7)	0.1310(−6)
	0.6961(+7)	0.4522(+4)	0.0	0.6965(+7)	0.1436(−6)
11	0.4400(+7)	0.5870(+4)	0.0	0.4406(+7)	0.2270(−6)
	0.4529(+7)	0.6698(+4)	0.0	0.4536(+7)	0.2205(−6)
	0.4533(+7)	0.5684(+4)	0.0	0.4539(+7)	0.2203(−6)
12	0.4276(+7)	0.9833(+4)	0.0	0.4286(+7)	0.2333(−6)
	0.4317(+7)	0.1056(+5)	0.0	0.4328(+7)	0.2311(−6)
	0.4240(+7)	0.1078(+5)	0.0	0.4251(+7)	0.2353(−6)
13	0.4456(+7)	0.8139(+4)	0.0	0.4464(+7)	0.2240(−6)
	0.4599(+7)	0.8450(+4)	0.0	0.4608(+7)	0.2170(−6)
	0.4302(+7)	0.9094(+4)	0.0	0.4312(+7)	0.2319(−6)
14	0.3705(+7)	0.8511(+4)	0.0	0.3714(+7)	0.2693(−6)
	0.3994(+7)	0.1052(+5)	0.0	0.4004(+7)	0.2497(−6)
	0.3830(+7)	0.8908(+4)	0.0	0.3839(+7)	0.2605(−6)
15	0.3192(+7)	0.1317(+5)	0.0	0.3206(+7)	0.3119(−6)
	0.3446(+7)	0.1696(+5)	0.0	0.3463(+7)	0.2888(−6)
	0.3414(+7)	0.1552(+5)	0.0	0.3429(+7)	0.2916(−6)

TABLE I. (*Continued.*)

K	$A(K-B)$	$A(K-C)$	$A(K-B')$	A	T
16	0.3125(+7)	0.1095(+5)	0.0	0.3136(+7)	0.3189(−6)
	0.3309(+7)	0.1415(+5)	0.0	0.3324(+7)	0.3009(−6)
	0.3230(+7)	0.1461(+5)	0.0	0.3245(+7)	0.3082(−6)
17	0.2945(+7)	0.1304(+5)	0.0	0.2958(+7)	0.3380(−6)
	0.3202(+7)	0.1420(+5)	0.0	0.3216(+7)	0.3110(−6)
	0.3072(+7)	0.1351(+5)	0.0	0.3086(+7)	0.3241(−6)
18	0.2279(+7)	0.2772(+5)	0.5416(+0)	0.2307(+7)	0.4335(−6)
	0.2973(+7)	0.1915(+5)	0.1350(−4)	0.2992(+7)	0.3342(−6)
	0.2871(+7)	0.1688(+5)	0.6419(−4)	0.2888(+7)	0.3462(−6)
19	0.1643(+7)	0.2216(+6)	0.9159(+3)	0.1865(+7)	0.5362(−6)
	0.2730(+7)	0.2025(+5)	0.5694(−5)	0.2750(+7)	0.3636(−6)
	0.2675(+7)	0.1823(+5)	0.3099(−3)	0.2693(+7)	0.3713(−6)
20	0.8794(+7)	0.2106(+7)	0.1760(+5)	0.1092(+8)	0.9159(−7)
	0.2840(+7)	0.7811(+6)	0.4518(+4)	0.3626(+7)	0.2758(−6)
	0.2417(+7)	0.6012(+6)	0.1655(+4)	0.3019(+7)	0.3312(−6)
21	0.3626(+8)	0.1159(+8)	0.1236(+6)	0.4798(+8)	0.2084(−7)
	0.4111(+8)	0.1351(+8)	0.1325(+6)	0.5475(+8)	0.1827(−7)
	0.4091(+8)	0.1292(+8)	0.8664(+5)	0.5392(+8)	0.1855(−7)
22	0.2313(+7)	0.2492(+5)	0.3607(+2)	0.2338(+7)	0.4278(−6)
	0.2556(+7)	0.1963(+5)	0.1376(−2)	0.2576(+7)	0.3882(−6)
	0.2512(+7)	0.1862(+5)	0.5051(−4)	0.2530(+7)	0.3952(−6)
23	0.2029(+7)	0.1114(+6)	0.2864(+4)	0.2144(+7)	0.4665(−6)
	0.2431(+7)	0.1909(+5)	0.9618(−2)	0.2450(+7)	0.4082(−6)
	0.2372(+7)	0.1836(+5)	0.5423(−2)	0.2391(+7)	0.4183(−6)
24	0.3508(+7)	0.4736(+7)	0.7962(+6)	0.9041(+7)	0.1106(−6)
	0.2574(+7)	0.5126(+7)	0.8533(+6)	0.8553(+7)	0.1169(−6)
	0.2635(+7)	0.5063(+7)	0.8422(+6)	0.8541(+7)	0.1171(−6)
25	0.7103(+7)	0.2700(+7)	0.2466(+5)	0.9828(+7)	0.1017(−6)
	0.1242(+8)	0.3583(+7)	0.2247(+5)	0.1602(+8)	0.6242(−7)
	0.1231(+8)	0.3492(+7)	0.9688(+4)	0.1581(+8)	0.6326(−7)
26	0.8330(+7)	0.2097(+7)	0.1927(+5)	0.1045(+8)	0.9572(−7)
	0.2309(+7)	0.2036(+5)	0.3220(−1)	0.2329(+7)	0.4293(−6)
	0.2241(+7)	0.1877(+5)	0.3980(−1)	0.2260(+7)	0.4425(−6)
27	0.5902(+7)	0.1494(+7)	0.2155(+5)	0.7418(+7)	0.1348(−6)
	0.2175(+7)	0.2190(+5)	0.2718(−1)	0.2197(+7)	0.4552(−6)
	0.2112(+7)	0.1963(+5)	0.7124(−1)	0.2132(+7)	0.4691(−6)
28	0.1574(+8)	0.4892(+7)	0.8545(+5)	0.2072(+8)	0.4827(−7)
	0.2296(+8)	0.7351(+7)	0.1050(+6)	0.3042(+8)	0.3287(−7)
	0.2236(+8)	0.6985(+7)	0.7432(+5)	0.2942(+8)	0.3399(−7)
29	0.3492(+7)	0.5261(+6)	0.1147(+5)	0.4030(+7)	0.2481(−6)
	0.2036(+7)	0.2227(+5)	0.1082(−1)	0.2058(+7)	0.4858(−6)
	0.1986(+7)	0.1993(+5)	0.3985(−1)	0.2006(+7)	0.4985(−6)
30	0.2571(+7)	0.5139(+5)	0.9895(+3)	0.2623(+7)	0.3812(−6)
	0.1903(+7)	0.2177(+5)	0.2229(+0)	0.1925(+7)	0.5194(−6)
	0.1864(+7)	0.1992(+5)	0.6864(−1)	0.1884(+7)	0.5309(−6)

TABLE I. (*Continued.*)

K	$A(K-B)$	$A(K-C)$	$A(K-B')$	A	T
31	0.1112(+8)	0.2204(+7)	0.3700(+6)	0.1369(+8)	0.7305(−7)
	0.1690(+8)	0.4580(+7)	0.3960(+5)	0.2152(+8)	0.4647(−7)
	0.1735(+8)	0.4740(+7)	0.3064(+5)	0.2212(+8)	0.4520(−7)
32	0.1379(+8)	0.9185(+7)	0.3229(+6)	0.2329(+8)	0.4293(−7)
	0.1070(+8)	0.7781(+7)	0.6903(+6)	0.1917(+8)	0.5217(−7)
	0.1143(+8)	0.7786(+7)	0.6593(+6)	0.1988(+8)	0.5031(−7)
33	0.4168(+7)	0.1319(+7)	0.1166(+5)	0.5499(+7)	0.1819(−6)
	0.1780(+7)	0.2082(+5)	0.7607(+0)	0.1801(+7)	0.5554(−6)
	0.1744(+7)	0.1942(+5)	0.4453(+0)	0.1763(+7)	0.5671(−6)
34	0.3246(+7)	0.8142(+6)	0.1245(+5)	0.4073(+7)	0.2455(−6)
	0.1661(+7)	0.2019(+5)	0.1151(+1)	0.1681(+7)	0.5948(−6)
	0.1625(+7)	0.1891(+5)	0.1048(+1)	0.1644(+7)	0.6084(−6)
35	0.1573(+8)	0.3562(+7)	0.6955(+5)	0.1936(+8)	0.5164(−7)
	0.1932(+8)	0.5221(+7)	0.8238(+5)	0.2462(+8)	0.4061(−7)
	0.1887(+8)	0.4969(+7)	0.5872(+5)	0.2389(+8)	0.4185(−7)
36	0.2621(+7)	0.5278(+6)	0.1270(+5)	0.3161(+7)	0.3163(−6)
	0.1541(+7)	0.1969(+5)	0.8941(+0)	0.1561(+7)	0.6407(−6)
	0.1504(+7)	0.1826(+5)	0.1256(+1)	0.1523(+7)	0.6568(−6)
37	0.4276(+7)	0.8260(+6)	0.4428(+5)	0.5146(+7)	0.1943(−6)
	0.1414(+7)	0.1913(+5)	0.6032(+0)	0.1433(+7)	0.6977(−6)
	0.1379(+7)	0.1750(+5)	0.9704(+0)	0.1396(+7)	0.7163(−6)
38	0.1146(+8)	0.1355(+7)	0.1269(+6)	0.1294(+8)	0.7727(−7)
	0.1684(+8)	0.4131(+7)	0.6338(+5)	0.2104(+8)	0.4753(−7)
	0.1689(+8)	0.4070(+7)	0.5103(+5)	0.2101(+8)	0.4759(−7)
39	0.6841(+7)	0.2210(+7)	0.1278(+6)	0.9179(+7)	0.1089(−6)
	0.1272(+7)	0.1810(+5)	0.1311(+1)	0.1290(+7)	0.7751(−6)
	0.1240(+7)	0.1639(+5)	0.9623(+0)	0.1257(+7)	0.7958(−6)
40	0.1936(+8)	0.9581(+7)	0.3651(+6)	0.2931(+8)	0.3412(−7)
	0.2405(+8)	0.1107(+8)	0.5842(+6)	0.3571(+8)	0.2800(−7)
	0.2668(+8)	0.1108(+8)	0.5294(+6)	0.3829(+8)	0.2612(−7)
41	0.3168(+7)	0.1186(+7)	0.1309(+5)	0.4367(+7)	0.2290(−6)
	0.1100(+7)	0.1628(+5)	0.2630(+1)	0.1116(+7)	0.8958(−6)
	0.1074(+7)	0.1472(+5)	0.1437(+1)	0.1089(+7)	0.9181(−6)
42	0.1037(+8)	0.2746(+7)	0.3348(+5)	0.1315(+8)	0.7605(−7)
	0.1257(+8)	0.2928(+7)	0.4116(+5)	0.1554(+8)	0.6436(−7)
	0.1319(+8)	0.3045(+7)	0.3543(+5)	0.1627(+8)	0.6147(−7)
43	0.7807(+6)	0.2512(+5)	0.4111(+3)	0.8063(+6)	0.1240(−5)
	0.8594(+6)	0.1308(+5)	0.3304(+1)	0.8724(+6)	0.1146(−5)
	0.8440(+6)	0.1189(+5)	0.1792(+1)	0.8559(+6)	0.1168(−5)
44	0.1010(+7)	0.2711(+6)	0.7067(+4)	0.1288(+7)	0.7765(−6)
	0.4047(+6)	0.6256(+4)	0.1980(+1)	0.4110(+6)	0.2433(−5)
	0.4100(+6)	0.5886(+4)	0.1136(+1)	0.4158(+6)	0.2405(−5)

The correlation between the index number k used in Table I to identify the upper states with the electronic-vibrational labels i,v' is defined and tabulated in Sec. III. Comparing the Born-Oppenheimer and adiabatic approximations in Table I we note that the transition probabilities, unlike the energies, are only weakly affected by the diagonal corrections, although these corrections yield energy shifts of up to 300 cm^{-1} for some of the levels.[10,15] This is because the electronic eigenfunctions are unaffected by the adiabatic corrections and the total transition probabilities are fairly insensitive to small redistributions among the individual $A_{iv',fv''}$ values owing to small changes in the vibrational wave functions.

III. NONADIABATIC CALCULATIONS

Nonadiabatic transition moments and lifetimes were obtained from nonadiabatic representations of the initial vibronic ${}^1\Sigma_g^+$ states while the final states B, B', and C were retained in the adiabatic approximation. We expand each vibronic ${}^1\Sigma_g^+$ state Ψ_k in the adiabatic basis $\Psi_{iv'}$:

$$\Psi_k=\sum_{i,v'}\Psi_{iv'}c_{iv',k} \; . \tag{6}$$

The summation includes the vibrational levels of the three electronic ${}^1\Sigma_g^+$ states $i=E,F,\ G,K,\ H,\bar{H}$.

The coefficients $c_{iv',k}$ were evaluated by separately computing adiabatic vibrational-electronic product functions

$$\Psi_{iv'}=\Psi_i(\vec{x}_1,\vec{x}_2;R)F_{iv'}(R) \; , \tag{7}$$

and nonadiabatic vibronic functions

$$\Psi_k=\sum_i\psi_i(\vec{x}_1,\vec{x}_2;R)F_{i,k}(R) \; . \tag{8}$$

Equations (6)–(8) were then combined to yield the coefficients $c_{iv',k}$ according to

$$c_{iv',k}=\langle\Psi_k\mid\Psi_{iv'}\rangle=\int F_{i,k}(R)F_{iv'}(R)dR \; . \tag{9}$$

The adiabatic vibrational wave functions $F_{iv'}(R)$ were computed using the adiabatically corrected potential functions. The nonadiabatic R-dependent expansion functions $F_{i,k}(R)$ were computed by solving the coupled equations for nuclear motion in a three-state approximation

$$\left[\underline{I}\frac{d^2}{dR^2}+2\underline{B}(R)\frac{d}{dR}+2\mu[E_k\underline{I}-\underline{V}(R)]+\underline{A}(R)\right]\vec{\text{F}}_k(R)=\vec{0} \; . \tag{10}$$

For each eigenvalue E_k the solution vector $\vec{\text{F}}_k(R)$ has three components $F_{i,k}(R)$ with $i=E,F,\ G,K,\ H,\bar{H}$, and all matrices in (10) are of dimension 3×3: The electronic energy matrix $\underline{V}(R)$ is diagonal with elements $V_i(R)$, the nuclear-momentum coupling matrix $\underline{B}(R)$ is antisymmetric with elements $B_{ij}(R)=\langle\psi_i\mid(d/dR)\mid\psi_j\rangle$, the diagonal elements of the matrix $\underline{A}(R)$ represent the nuclear-motion corrections $-(1/2\mu)A_{ii}(R)$ to the electronic energies $V_i(R)$,

$$A_{ii}(R)=\left\langle\psi_i\left|\left[\frac{d^2}{dR^2}-\frac{L^+L^-}{R^2}+\tfrac{1}{4}(\nabla_1+\nabla_2)^2\right]\right|\psi_i\right\rangle , \tag{11}$$

the off-diagonal elements of $\underline{A}$ have been computed in the approximation

$$A_{ij}(R)=\left\langle\psi_i\left|\left[\frac{d^2}{dR^2}-\frac{L^+L^-}{R^2}\right]\right|\psi_j\right\rangle , \tag{12}$$

and $\underline{I}$ is the unit matrix. The coupling functions $B_{ij}(R)$ and $A_{ij}(R)$ between the E,F and G,K states are taken from Ref. 19, and between the G,K and $H,\bar{H}$ states they are

TABLE II. Nonadiabatic coupling functions A_{ij} defined in Eq. (12), $B_{ij}=\langle i\mid(d/dR)\mid j\rangle$, $G_{ij}=\frac{1}{4}\langle i\mid(\nabla_1+\nabla_2)^2\mid j\rangle$ (see Ref. 19 for further details; all values in a.u.), and overlap integrals $S_{ij}=\langle i\mid j\rangle$, computed with 40-term wave functions $\psi_i=\psi_{H,\bar{H}}$ from Refs. 11 and 15, and $\psi_j=\psi_{G,K}$ from Refs. 10 and 19.

R	A_{12}	A_{21}	B_{12}	B_{21}	G_{12}	S_{12}
2.0	0.5747	0.1335	−0.0900	0.0833	0.002 759	−0.0072
2.25	0.1093	0.4629	−0.1085	0.1583		−0.0128
2.5	−0.8244	1.0749	−0.2274	0.3169	0.005 886	−0.0101
2.625	−0.8688	1.8339	−0.3746	0.4645		−0.0197
2.75	−0.9220	3.1186	−0.6000	0.6795		−0.0133
2.8125	−0.4169	3.7157	−0.7362	0.7968		−0.0075
2.875	+0.7042	3.6925	−0.8539	0.8920		−0.0026
2.9375	2.0490	2.4663	−0.9061	0.9266		+0.0010
3.0	2.9199	0.4175	−0.8609	0.8758	0.033 85	+0.0038
3.0625	1.9466	−1.0211	−0.5239	0.7662		−0.0406
3.125	2.0757	−1.7603	−0.4423	0.6253		−0.0297
3.25	1.6138	−1.4263	−0.2596	0.3479		−0.0161
3.375	0.8705	−0.8604	−0.1304	0.1731		−0.0098
3.5	0.4053	−0.5445	−0.0542	0.0780		−0.0070
3.75	0.0675	−0.2995	+0.0261	−0.0102		−0.0054

TABLE III. Elements $c_{iv',k}$ of the vector C_k for $k=20$, i.e., the perturbed G,K, $v=0$ level, and transition moment integrals $M_{iv',B0}$ (a.u.) to the lower state $B\,^1\Sigma_u^+$, $v''=0$. Numbers in parentheses indicate factors of 10, e.g., $0.5(+2)=0.5\times10^2$.

I	v'	$C_{iv',k=20}$	$M_{iv',v''=0}$
E,F	0	−0.000 591	0.130 678(+ 1)
	1	0.002 001	0.237 548(− 1)
	2	−0.004 174	−0.589 385(− 1)
	3	−0.004 064	0.133 288(+ 1)
	4	0.006 105	0.436 789(− 1)
	5	−0.005 410	−0.178 524(+ 0)
	6	−0.013 467	0.867 998(+ 0)
	7	0.009 628	−0.188 487(+ 0)
	8	0.005 532	−0.143 659(+ 0)
	9	−0.025 817	0.273 561(+ 0)
	10	0.019 042	−0.148 145(+ 0)
	11	0.003 734	0.165 108(− 1)
	12	−0.025 912	0.438 697(− 1)
	13	0.033 617	−0.531 090(− 1)
	14	−0.019 678	0.315 811(− 1)
	15	−0.009 124	−0.749 865(−2)
	16	0.048 508	−0.829 377(−2)
	17	−0.104 633	0.140 048(− 1)
	18	0.609 939	−0.121 198(− 1)
	19	0.027 669	0.691 258(−2)
	20	0.016 260	−0.162 133(−2)
	21	−0.022 713	−0.217 329(−2)
	22	0.019 453	0.404 970(−2)
	23	−0.013 164	−0.428 052(−2)
	24	0.006 822	0.345 629(−2)
	25	−0.001 756	−0.217 677(−2)
	26	−0.001 652	0.883 255(−3)
	27	0.003 523	0.173 070(−3)
	28	−0.004 190	−0.894 608(−3)
	29	0.004 045	0.128 328(−2)
	30	−0.003 443	−0.139 179(−2)
	31	0.002 652	0.127 599(−2)
	32	−0.001 705	−0.864 108(−3)
G,K	0	0.738 697	0.304 566(+ 0)
	1	−0.233 420	−0.918 497(+ 0)
	2	0.038 080	−0.113 331(+ 0)
	3	0.059 277	0.242 507(+ 0)
	4	0.004 766	−0.113 573(+ 0)
	5	−0.038 148	0.248 872(− 1)
	6	0.013 883	0.195 401(− 1)
	7	0.010 594	−0.242 265(− 1)
	8	−0.014 544	0.160 771(− 1)
$H,\bar{H}$	0	−0.004 032	−0.301 268(+ 0)
	1	−0.002 556	−0.548 323(+ 0)
	2	−0.003 981	−0.523 107(+ 0)
	3	0.002 576	−0.293 020(+ 0)
	4	0.005 136	−0.162 018(− 1)

presented in Table II. The direct coupling between the E,F and $H,\bar{H}$ states is neglected; it is expected to be very small because the diagonal term $A_{ii}(R)$ for the E,F state agrees well with $-|B_{ij}(R)|^2$ for $i,j=E,F$ and G,K, such that B_{ik} must be small for $i=E,F$ and $k\neq G,K$ as discussed in Ref. 19.

The coupled equations (10) have been solved by the renormalized Numerov method as developed by Johnson[20] after transformation into a diabatic electronic basis [$\underline{B}(R)=\underline{0}$; $\underline{V}(R)$ nondiagonal]. The resulting diabatic oscillator functions have subsequently been transformed back into the adiabatic representation $\vec{F}_k(R)$ of Eq. (10).

The coefficients $c_{iv',k}$ have been calculated for $v'=0,\ldots,v^i_{\max}$, where for $i=E,F$ and G,K, $v^i_{\max}$ is the quantum number of the highest bound adiabatic vibrational level, while for $i=H,\bar{H}$, we used $v^i_{\max}=4$. (The levels $v=0$–4 lie in the inner well of the $H,\bar{H}$ double-minimum potential function.) As an example of a vector of coefficients $c_{iv',k}$ we list $\vec{C}_k$ for $k=20$ in Table III.

Nonadiabatic transition moments $M_{k,fv''}$ are calculated by the transformation

$$M_{k,fv''}=\sum_{i,v'}M_{iv',fv''}c_{iv',k}=\vec{M}_{fv''}\cdot\vec{C}_k\ . \tag{13}$$

Nonadiabatic transition probabilities $A_{k,fv''}$ are obtained after substitution of $M_{k,fv''}$ from Eq. (13) in place of $M_{iv',fv''}$ and of E_k from Eq. (10) in place of E_{iv}, in Eq. (3), and the nonadiabatic lifetimes then follow from Eq. (4) after substitution of $A_{k,fv''}$ in place of $A_{iv',fv''}$:

$$1/\tau_k=A_k=\sum_{f,v''}A_{k,fv''}\ . \tag{14}$$

Special attention has been paid to the determination of appropriate signs within each vector $\vec{C}_k$ relative to the signs within each vector of transition moments $\vec{M}_{fv''}=(M_{iv',fv''})$ in order to represent the interferences in the transformation (13) correctly. While the overall signs of $\vec{M}$ and of $\vec{C}_k$, and hence, of $M_{k,fv''}$ are arbitrary, the relative signs of the elements $M_{iv',fv''}$ within the vector $\vec{M}$ as well as the relative signs of the elements $c_{iv',k}$ within the vector $\vec{C}_k$ are determined by the sequence of signs chosen for the vibrational functions $F_{iv'}(R)$ [cf. Eq. (9)]. The relative signs of the three components $F_{i,k}(R)$ which occur in (9) are determined by the coupled equations (10), and the overall sign of each $\vec{C}_k$ is arbitrarily chosen such that the largest component is positive. The sign of each vibrational wave function $F_{iv'}(R)$ has been set such that the wave at *largest* R, i.e., in the *outer* classically forbidden region, is positive. It is important to adhere strictly to this latter convention in any computations of properties of the nonadiabatic states based on transformations of adiabatically computed properties with vectors $\vec{C}_k$ such as the one listed in Table III.

The nonadiabatic transition probabilities and lifetimes are presented in Table I. Available experimental lifetimes are compared with the nonadiabatically computed ones in Table IV. This table also permits the correlation between the index k used in Table I and the electronic-vibrational labels iv' of the Born-Oppenheimer and adiabatic representations.

Comparison of the adiabatic and nonadiabatic transition probabilities in Table I shows that the results are particularly sensitive to the nonadiabatic interaction for those levels whose energies and rotational structures are known to be strongly affected by these interactions,[19] such as,

TABLE IV. Correlation between spectroscopic labels, and comparison between measured and nonadiabatically computed lifetimes.

k	Dieke name[d]	Crosswhite name[e]	Spectroscopic name i	v	Measured lifetime (ns)	N-A calculated lifetimes (ns)
1	2*A* 0	2*A* 0	*E,F*	0		203.0
2			*E,F*	1		1144.0
3			*E,F*	2		664.0
4			*E,F*	3		139.0
5			*E,F*	4		453.0
6			*E,F*	5		317.0
7	2*A* 2	2*A* 2	*E,F*	6	100.0(20.0)[a]	99.5
8	2*K* 0	2*K* 2	*E,F*	7		256.0
9	2*K* 1	2*K* 3	*E,F*	8		176.0
10	2*A* 3	2*A* 3	*E,F*	9		131.0
11	2*K* 2	2*K* 4	*E,F*	10		227.0
12	2*K* 3	2*K* 5	*E,F*	11		233.0
13	2*A* 4	2*A* 4	*E,F*	12		224.0
14	2*K* 4	2*K* 6	*E,F*	13		269.0
15			*E,F*	14		312.0
16			*E,F*	15		319.0
17			*E,F*	16		338.0
18			*E,F*	17		433.0
19	*Q* 0	*V* 0	*E,F*	18		536.0
20	3*K* 0	*Z* 0	*G,K*	0	76.0(6.0)[b]	91.6
21	3*D* 0	3*D* 0	*G,K*	1	24.8(4.0)[b] 28.2(1.7)[c]	20.8
22	*Q* 1	*V* 1	*E,F*	19		428.0
23			*E,F*	20		467.0
24	3*A* 0	3*A* 0	*H,H*	0		111.0
25	*L* 0	*Y* 1	*G,K*	2		102.0
26	*M* 0	*X* 0	*E,F*	21	89.8(7.0)[b]	95.7
27	3*K* 1	*Z* 1	*E,F*	22	~100.0[b]	135.0
28	3*D* 1	3*D* 1	*G,K*	3	36.1(2.1)[c] 39.5(1.9)[b]	48.3
29	*U*	*U* 1	*E,F*	23		248.0
30			*E,F*	24		381.0
31	*N* 0	*W* 1	*G,K*	4	50.4(4.0)[b]	73.1
32	3*A* 1	3*A* 1	*H,H*	1		42.9
33	*M* 1	*X* 1	*E,F*	25		182.0
34	3*K* 2	*Z* 2	*E,F*	26	48.5(3.0)[c]	245.0
35	3*D* 2	3*D* 2	*G,K*	5	47.3[c] 48.9(4.0)[b]	51.6
36			*E,F*	27		316.0
37	*L* 1	*Y* 2	*E,F*	28		194.0
38	*N* 1	*W* 2	*G,K*	6	64.0(5.0)[b]	77.3
39	4*K* 0	*T*	*E,F*	29		109.0
40	3*A* 2	3*A* 2	*H,H*	2		34.1
41	*M* 2	*X* 2	*E,F*	30		229.0
42	3*D* 3	3*D* 3	*G,K*	7	29.2(1.8)[c] 32.1(2.6)[b]	76.0
43			*E,F*	31		1240.0
44			*E,F*	32		776.0

[a] Reference 3.
[b] Reference 4.
[c] Reference 2.
[d] Reference 21.
[e] Reference 22.

e.g., the perturbed level $k=20$ (G,K, $v=0$), where the discrepancy between calculation and experiment (Table IV) is much reduced by the nonadiabatic treatment.

It must be noted that the experimental results (Table IV) were all obtained for $J'=1$ levels, while the calculation presented here is valid only for the $J'=0$ levels. The corresponding calculation for the $J'=1$ levels will have to include the nonadiabatic coupling of the ${}^1\Sigma_g^+$ states with ${}^1\Pi_g^+$ states (and with ${}^1\Delta_g^+$ states for the levels with $J'>1$).

The largest discrepancies remaining in Table IV involve the levels $k=34$ and 42 which lie very close to the levels $I\,{}^1\Pi_g^+$, $v=2$ and 3, respectively; therefore, these levels may be strongly affected by the heterogeneous Σ^+-Π^+ mixing. Results of calculations including the states $I\,{}^1\Pi_g^+$ and $J\,{}^1\Delta_g^+$ and complete tables of vibronic transition moments $M_{iv',fv''}$ eigenvectors $\vec{C}_k$, and transition probabilities $A_{k,fv''}$ will be published later.

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